Radiation Polymerization

Grafting

Grafting

- Chemical bonding of a monomer, to a polymer, by a polymerizing reaction
- Results in a polymer with short chains of another polymer on its surface
- A good method to change surface properties of a polymer
- Products include specialty textiles (wrinkle- or fire-resistant), battery separators, immobilized biomaterials, slow-release drugs

Grafting Methods

- Pre-irradiation

$$RH \xrightarrow{\sim\sim} R^{\bullet} + H^{\bullet}$$

$$H^{\bullet} + RH \longrightarrow R^{\bullet} + H_2$$

$$R^{\bullet} + M \longrightarrow RM^{\bullet} \rightarrow \text{Grafted Polymer}$$

- Peroxidation

$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet}$$

$$RO_2^{\bullet} + RH \longrightarrow ROOH + R^{\bullet}$$

$$ROOH \text{ or } RO_2^{\bullet} + M \rightarrow \boxed{\text{Extrusion Injection moulding}} \rightarrow \text{Grafted Polymer}$$

Grafting Methods (contd)

- Simultaneous irradiation

$$RH \xrightarrow{\sim\sim} R^{\bullet} + H^{\bullet}$$

$$R^{\bullet} + M \longrightarrow RM^{\bullet}$$

$$RM^{\bullet} + nM \longrightarrow RM^{\bullet}_{n+1} \qquad \text{Grafted polymer}$$

$$M \xrightarrow{\sim\sim} M^{\bullet} + H$$

$$M^{\bullet} + nM \longrightarrow M^{\bullet}_{n+1}$$

$$R^{\bullet} + M^{\bullet}_{n+1} \longrightarrow RM_{n+1} \qquad \text{Grafted polymer}$$

Variables Affecting Grafting Yields

- ***Solvent***
  - **Grafting yields may depend on the solvent, and on any additives present**

Effect of Monomer Concentration, and Acid, on the Grafting Yield (%) of Styrene on Polypropylene, on Irradiation to 3 kGy

Solvent	Styrene (%)			
	20	20[a]	40	40[a]
Methanol	29	214	50	86
Ethanol	44	176	65	72
n-Butanol	123	214	34	83
n-Octanol	49	154	68	128
Dimethylformamide	24	32	43	56
Dimethylsulfoxide	11	17	66	93
Acetone	13	20	24	32
1,4-Dioxane	6	14	15	30

[a] The solution contains 0.2 mol.dm^{-3} H_2SO_4, (Dworjanyn and Garnett , 1992)

Variables Affecting Grafting Yields (contd)

Comparison of Acid with Polyfunctional Monomers for Enhancing Grafting Yield (%) of Styrene to Polyethylene Film on Irradiation to 2.4 kGy

Additives[a]	Styrene (%) in Methanol			
	20	30	40	50
None	14	37	76	109
H^+	19	51	81	134
DVB	15	41	74	136
DVB + H^+	27	58	119	188
TMPTA	--	39	73	137
TMPTA + H^+	--	54	106	181

[a] H^+, 0.20 mol.dm^3 H_2SO_4; divinylbenzene (DVB) and trimethylolpropane triacrylate (TMPTA) at 1 vol %

Dworjanyn and Garrett, 1992

Variables Affecting Grafting Yields (contd)

- *Dose Rate*

  $RH \xrightarrow{\sim\sim} R\cdot + H\cdot$

  $M \xrightarrow{\sim\sim} M\cdot + H\cdot$

  - At low dose rates

    $R\cdot + M \longrightarrow RM\cdot$

  - At high dose rates

    $R\cdot + R\cdot \longrightarrow R\text{-}R$

    $M\cdot + M\cdot \longrightarrow M\text{-}M$

- At high dose rates crosslinking of the polymer and homopolymerization of the monomer are favoured over grafting

Effect of Dose Rate on Grafting Yield (%) of Styrene to Polyethylene from Methanol Solution

(Dworjanyn and Garnett, 1992)

Styrene (%)	100 Gy/h	410 Gy/h	1120 Gy/h
20	24	14	7
30	61	37	14
40	51	76	23
50	409	109	25

Grafting on Textiles

- Cotton/Polyester Material
  - N-Methylolacrylamide grafting reduces electrostatic charging, gives the material permanent-press and non-wrinkle properties (electron irradiation process introduced in USA in 1960)
- Cotton Fabrics
  - Grafting with fluorinated acrylates and silicones makes them water-repellant
  - Grafting with vinyl bromide triallyl phosphate and vinyl phosphonate oligomers makes them fire-retardant

Woods and Pikaev (1994)

Other Products

- Oil Resistance
  - Radiation grafting of acrylic acid and acrylonitrile improves oil resistance of butadiene-styrene copolymer, and of ethylene-propylene-diene terpolymer
- Encapsulated Fertilizer
  - Successive radiation grafting of methyl methacrylate, followed by vinylidene chloride, on carbamide (carbamide/polymer, 95/5) to a dose of ~ 30 kGy, results in slow-acting (≥ 30 days) fertilizer

Conclusions

- The use of radiation processing for grafting would continue to grow
- This is primarily an application for low energy electron accelerators (~0.3 MeV)